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**by**

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# Photofabrication of surface relief gratings on azobenzene polymer films

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## ABSTRACT

Surface relief gratings were photofabricated on various polymer films containing azobenzene groups in the side chain or in the main chain. Formation of the surface relief gratings on the polymer was very sensitive to the polymer structures. The surface gratings were produced on the polymers containing photoisomerizable azobenzene groups. Recording of the gratings was strongly dependent on the polarization of the beams. The localized variations of magnitude and polarization of the resultant electric field in the film are essential to the formation of the surface relief gratings. Large surface modulation ( $>6000 \text{ \AA}$ ) and high diffraction efficiency ( $>40\%$  into each of  $\pm 1$  order) were obtained under optimal recording conditions. The diffraction efficiency of the surface relief grating was dependent only on the total light energy incident on the film. The surface pattern resulting from straight edge diffraction mapped the negative first derivative of the intensity distribution. Fabrication of various multiple gratings on the same spot of the polymer films were demonstrated. Fourier blazed gratings were also fabricated. The resulting surface pattern was a simple superposition of all the interfering recording waves.

**Keywords:** surface relief gratings, polymer, surface modulation, azobenzene, polarization, diffraction efficiency, multiple gratings, photoisomerization, Fourier blazed gratings

## 1. INTRODUCTION

It has been known over a decade that azobenzene groups in polymer matrices give rise to optical birefringence when excited by polarized light.<sup>1-5</sup> This process involves repeated trans-cis photo-isomerization and thermal cis-trans relaxation of azobenzene groups, which result in orientation of the azobenzene groups perpendicular to the polarization direction of the incident beam. This photoinduced orientation of azobenzene groups has been studied in various polymer matrices and also employed to produce birefringence gratings by a number of research groups.<sup>1-3</sup> However, surface relief grating formation has only been reported by us<sup>6-9</sup> and independently by Natansohn and Rochon<sup>10-11</sup> very recently.

We have reported direct formation of large amplitude ( $>1000 \text{ \AA}$ ) holographic surface relief gratings on epoxy-based NLO polymer films containing azobenzene groups.<sup>6-9</sup> These surface relief gratings were produced upon exposure to an interference pattern of  $\text{Ar}^+$  laser beams at modest intensities without any subsequent processing steps. The gratings were very stable when the polymer was kept below the glass transition temperature ( $T_g$ ). The gratings could be erased by heating the polymer above  $T_g$ . It is certain that during the recording process, photo-induced large scale molecular motion is occurring, which cannot be explained solely by the reorientation of the azo chromophores. Since only the functionalized polymers with the azo chromophores which can participate in the trans-cis-trans photoisomerization could give rise to significant surface relief grating,<sup>6-11</sup> it is believed that the photoisomerization certainly plays a principal role in the formation of surface relief gratings. To explore this novel process, various factors such as the chemical structures of the polymers and the exposure conditions should be carefully examined. Since this surface grating formation process provides the single step processing and the large surface variation on the polymer films, such polymers are expected to have significant potential applications for various optical devices and optical elements.

In this paper, we report the photo-induced surface relief grating formation in various polymer films containing azobenzene groups in the side chain or in the main chain. We also report the effects of the various exposure conditions including polarization and energy dependence on the grating recording process. Fabrication of various multiple gratings on the same spot of the polymer films were demonstrated. Fourier blazed gratings were also fabricated.

## 2. EXPERIMENTAL

Figure 1 shows chemical structures of the polymers on which the surface grating formation was investigated.

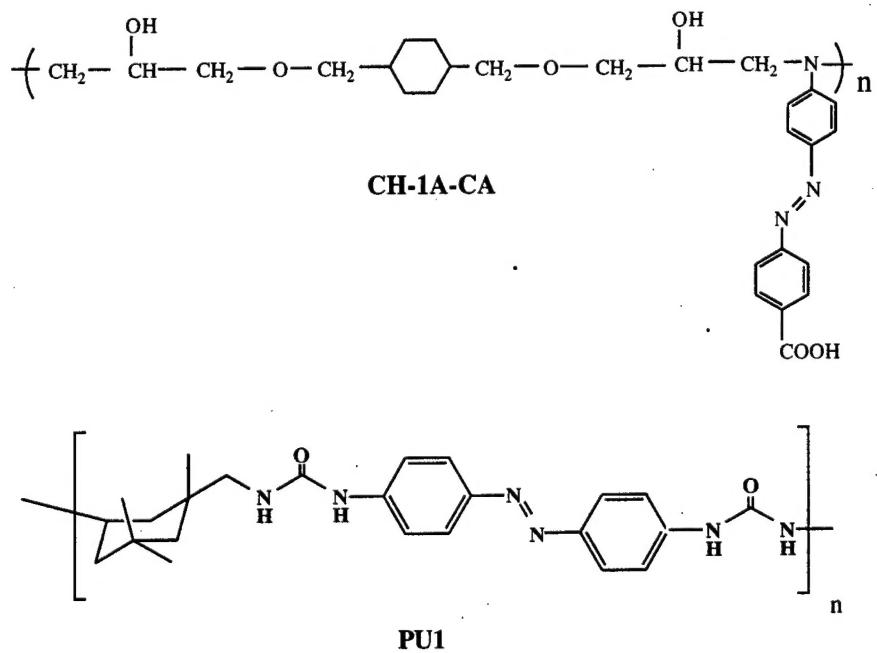
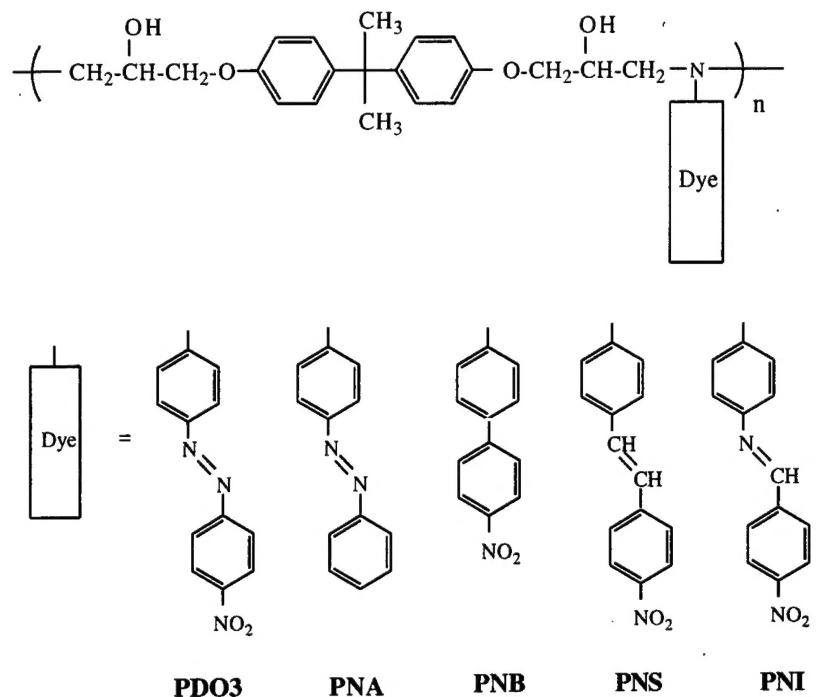


Fig. 1. The chemical structures of the polymers on which the surface grating formation was investigated.

All the side chain polymers, PDO3, PNA, PNB, PNS, and PNI, were synthesized by reacting diglycidyl ether of bisphenol A and various chromophores according to the procedures reported earlier.<sup>12</sup> The Tgs of these polymers were about 100 °C. An azo polymer CH-1A-CA was synthesized by post azo coupling reaction.<sup>13</sup> The Tg of the polymer was 93 °C.

A main chain azo polymer PU1 was synthesized from the reaction of diaminoazobenzene and isophorone diisocyanate.<sup>14</sup> The T<sub>g</sub> of the PU1 was 197 °C. All these polymers were amorphous. Good optical quality polymer films were prepared by spin-casting on glass slides. The films were dried at 70 °C under vacuum for 12 hours. The typical sample thickness of the films was ranging from 0.4 to 0.8  $\mu\text{m}$ .

The experimental setup for the grating formation is shown in Fig. 2 (a).<sup>9</sup> A linearly polarized laser beam at 488 nm from an Ar<sup>+</sup> laser was used. The polarized laser beam passed through a halfwave plate, and then was expanded and collimated. Half of the collimated beam passes through another halfwave plate and is incident on the sample directly. The other portion of the beam is reflected onto the sample from a mirror. Laser beams with various polarizations (defined by an angle  $\alpha$ , which is half of the angle between two polarization respect to s-polarization) were achieved by rotating the first halfwave plate. By replacing the halfwave plate with a quarter wave plate, a circularly polarized beam could be obtained. By selecting either  $\alpha=0^\circ$  or  $\alpha=90^\circ$  and positioning the second halfwave plate in one of the recording beams, two orthogonally polarized recording beams could be obtained. This recording condition is called polarization recording in this paper. The intensity of the recording beam employed ranged from 3 to 110 mW/cm<sup>2</sup>. In the polarization dependence study, a laser beam with an intensity of 55 mW/cm<sup>2</sup> was used and the recording time was about 45 minutes. In most cases, the incident angle  $\theta$  of the recording beams was selected to be 14°, resulting in grating spacing of about 1  $\mu\text{m}$  otherwise mentioned. The diffraction efficiency of the first order diffracted beam from the gratings in transmission mode was probed with an unpolarized low power He-Ne laser beam at 633 nm.

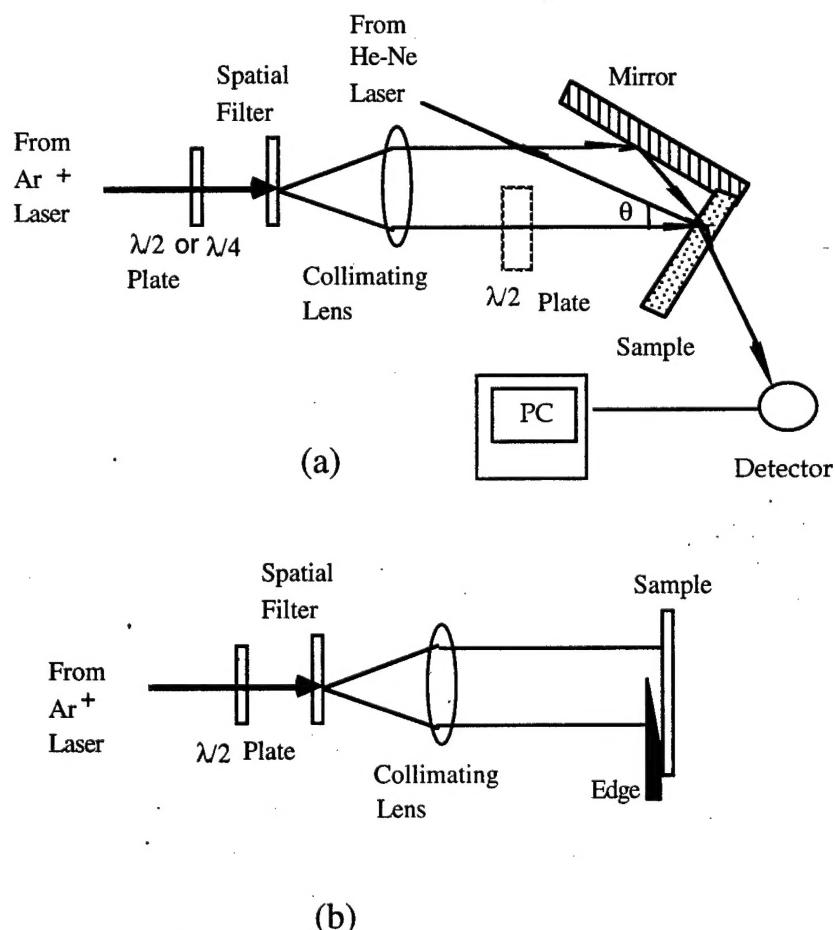


Fig. 2. Experimental setup for (a) the grating recording, and (b) the edge diffraction pattern recording.

To study the dependence of the formation of surface relief gratings on the recording intensity and energy, the gratings were recorded at four different intensities viz., 110, 55, 10, and 3 mW/cm<sup>2</sup> respectively. The recording time was chosen so that the total incident energy in the four cases was comparable and the diffraction efficiency values were not saturated. The recording condition,  $\alpha=45^\circ$ , was used in this experiment.

To investigate the relation between the light intensity distribution and the surface deformation pattern, a straight edge diffraction experiment was performed as shown in the Fig. 1 (b). The space between the edge and the film is about 100  $\mu\text{m}$ . The film was irradiated by the laser beam with two different polarization, parallel and perpendicular to the edge. The intensity of laser beam was about 110 mW/cm<sup>2</sup>.

To form orthogonal double gratings, PDO3 film was exposed to a p-polarized beam at 488 nm and after rotation of the sample by 90°, the sample was re-exposed under the same condition. In the case of the grating with a beat structure, the PDO3 film was sequentially exposed to beams with two different wavelength, one at 488 nm and the other at 514 nm at a fixed writing angle. For Fourier blazed grating formation, two gratings, one with a spacing of  $\Lambda_g$  and the second one at half of  $\Lambda_g$ , were recorded sequentially at two different writing angles.

### 3. RESULTS AND DISCUSSION

Surface relief gratings with large surface modulations could be formed on the polymers with azobenzene side groups, such as PDO3, PNA and CH-1A-CA.<sup>7,8</sup> Surface relief gratings on polymer films were investigated by atomic force microscopy (AFM). A typical three-dimensional view of the surface gratings on the polymer, PDO3, is shown in Fig. 3.

As shown in Fig. 3, the surface gratings showed very regularly spaced sinusoidal surface relief structures with a depth modulation of over 1000 Å. The original film surfaces before exposure to the writing beams were planar with just tens of angstroms fluctuations in the depth without any regular periodicity. The grating spacing could be controlled by changing the angle ( $2\theta$ ) between the two writing beams and was consistent with the theoretically calculated spacing for the interference pattern. It is clear that the surface relief patterns were produced by the interfering laser beams. Under the optimum condition, surface modulation depth greater than 6000 Å could be produced.

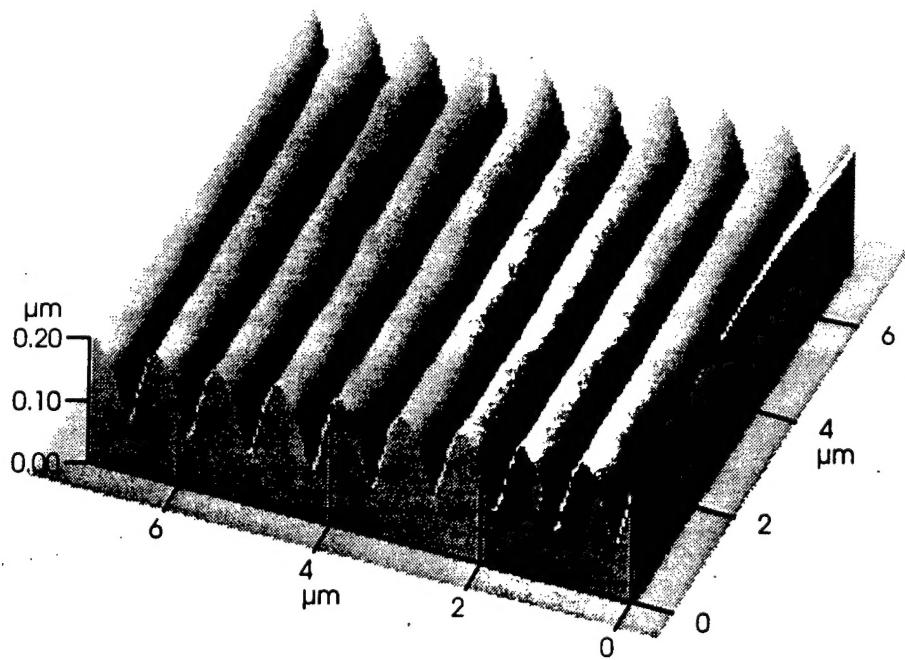


Fig. 3. A Typical AFM 3-D view of the surface relief grating on the PDO3 film.

Among the side chain azo polymers, PDO3, PNA, and CH-1A-CA showed the formation of large surface relief gratings. In case of the biphenyl side chain polymer, PNB, surface grating was barely observed under the same exposure level. When it is considered that the polymer PNB has the same backbone structure as PDO3 and PNA, we can infer that the presence of azobenzene side groups which can undergo *trans-cis* photoisomerization is a critical structural requirement for the surface deformation process. PNA was less efficient for surface grating formation than PDO3. It may be attributed to lower optical density of PNA at the writing wavelength. Furthermore the acceptor substituted azo chromophore is expected to have a shorter excited state lifetime and hence cycle more often in the same time frame. It appears that strong electron donor-acceptor structure of the chromophore is helpful but is not a critical factor for the surface grating formation. The polymer CH-1A-CA, which is a water-soluble (alkaline pH) polymer, also showed as efficient surface grating formation as the PDO3.

We also investigated the polymers with stilbene (PNS) and imine chromophores (PNI). These chromophores are known to be able to undergo *trans-cis* photoisomerization process as well. However, the amplitude of surface grating produced was not appreciable in these polymer films. In addition, photo-induced orientation process of chromophores was not observed with these polymer films. It is probably because both stilbene and imine groups require larger free volume (about  $224 \text{ \AA}^3$ ) for the photoisomerization compared to the azobenzene groups ( $127 \text{ \AA}^3$ ).<sup>15</sup> In these type of moderately high Tg polymer matrix, there may not be enough free volume for the photoisomerization of the stilbene and imine chromophores. Therefore, we conjecture that the photo-induced orientation process is quite an important factor in the surface deformation process.

Surface relief gratings could be fabricated on the film of the main chain azo polyurea, PU1. As expected, the formation of the surface grating was much slower than the side chain polymers as the polymer has a rigid backbone and the azobenzene groups are bound to the backbone at both ends which restrict the mobility of the azo chromophores. However, when it is considered that this main chain polymer has very high Tg, and relatively low absorption at the writing wavelength compared to the side chain polymers, the observation of the surface modulation was quite remarkable. We are currently investigating other series of azo polymers to further explore the effects of the structures on the surface grating formation.

A typical diffraction efficiency curve of the grating on the PDO3 film monitored at 633 nm during the writing process is shown in Fig. 4. The photoinduced orientation effects leading to refractive index and orientation gratings contributed to the initial increase of the diffraction efficiency. The following stage might involve the saturation of orientation grating and partial cancellation of the refractive index grating by the surface modulation.<sup>7</sup> In the later stage, the diffraction efficiency increased almost linearly until saturation. The increase of diffraction efficiency after the first minute or so of recording indicates the formation process of the surface relief grating. Under optimal conditions, diffraction efficiency higher than 40 % into each  $\pm 1$  order could be achieved.

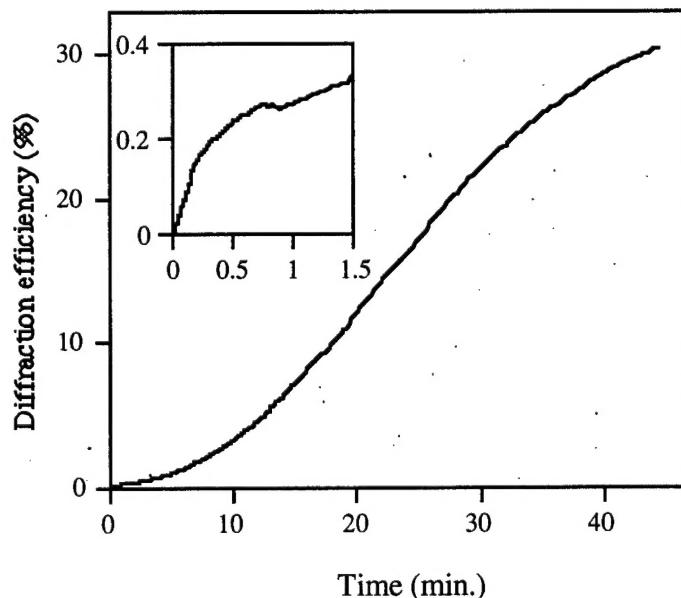


Fig. 4. A typical diffraction efficiency of the grating on PDO3 film as a function of time under recording condition,  $\alpha=45^\circ$ . The inset shows the initial stages of the grating formation.

Polarization states of the writing beams significantly influenced the grating formation process.<sup>7,9,11</sup> The diffraction efficiencies and surface modulations of the surface relief gratings recorded on the PDO3 film under different polarization of recording beam are summarized in Table I. All diffraction efficiency values in the table were measured at least one day after the gratings were recorded to ensure that there are no transient effects involved.

Table I. The diffraction efficiency and surface modulation under different recording conditions.

| Recording conditions   | Diffraction efficiency (%) | Surface modulation (Å) |
|------------------------|----------------------------|------------------------|
| $\alpha = 0^\circ$     | < 0.01                     | < 100                  |
| $\alpha = 45^\circ$    | 27                         | 3600                   |
| $\alpha = 90^\circ$    | 15                         | 2540                   |
| Circularly polarized   | 30                         | 3500                   |
| Polarization recording | < 0.05                     | < 100                  |

Under the condition for intensity recording ( $\alpha=0^\circ$ , two s-polarization), interference of the two recording beams with parallel polarization gives rise to the largest light intensity variation. However, the resultant electric field is always linearly polarized and in the direction parallel to the grating grooves over the entire irradiated area (i.e., there is no spatial alternation of direction of the resultant electric field and no component of resultant electric field along the intensity gradient). Very low diffraction efficiency and small surface modulation (<100 Å) were obtained from the grating recorded.

Under the polarization recording condition, resulting from the superposition of the two recording beams with orthogonal polarization, the greatest alternation of the resultant electric field polarization occurs on the film surface. However, the light intensity on the film is uniform over the entire irradiated area. Very small surface modulation and diffraction efficiency were also obtained under this recording condition. As the orientation grating formed, the diffraction efficiency increased, saturated and remained at a constant value throughout the rest of the recording process. After the laser beams were switched off, the diffraction efficiency decayed nearly to zero, indicating that most of the orientation grating had disappeared.

Under the other recording conditions, variations of both light intensity and the resultant electric field polarization on the film exist simultaneously. Surface relief gratings could be formed, leading to much greater values of surface modulation and diffraction efficiency than those from intensity recording and from polarization recording alone. This seems to indicate that the existence of both light intensity and resultant electric field polarization variations is essential to the formation of surface relief gratings. Under the recording condition of  $\alpha=45^\circ$ , a diffraction efficiency higher than 40 % and the maximum surface modulation greater than 6000 Å were obtained. The gratings recorded with circularly polarized laser beams also revealed large surface modulations with high diffraction efficiencies.

Fig. 5 displays the diffraction efficiencies as function of energy with different intensities of the recording beam under the writing condition of  $\alpha=45^\circ$ . Within the intensity range, the diffraction efficiency of the gratings is dependent only on the energy. It clearly shows that the surface grating formation process is not a thermal effects. This also suggest that the recording rate of the grating is proportional to the intensity and thus, to the rate of the photoisomerization. In the photoisomerization process, an azobenzene group would undergo repeated trans-cis-trans cycling until its orientation is perpendicular to the polarization of light. In some recording condition such as  $\alpha=90^\circ$  (two p-polarized beams), the photoisomerization could buildup a spatially varied distribution of the azobenzene group alignment. This can lead to a decrease of the photoisomerization rate. In the optimal condition, the photoisomerization process does not induce a temporary stable distribution of azobenzene group alignment. The total number of photoisomerization cycles under this condition would be much larger than that under the exposure condition of  $\alpha=90^\circ$ . This might explain why with the same irradiation energy, the surface modulations formed under this condition are larger than the already efficient writing condition of  $\alpha=90^\circ$ .

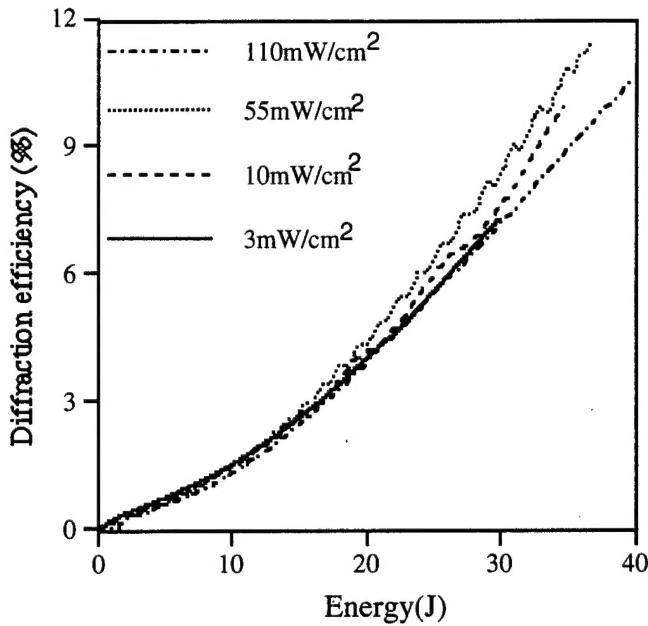


Fig. 5. Diffraction efficiency of the surface grating as functions of recording power and energy.

To investigate the phase relationship between the diffraction pattern of the writing beams and the surface deformation patterns, a straight edge diffraction experiment was performed. Similar to the result of the grating recording with s-polarized beam, when the polarization of the irradiation beam is parallel to the edge, no regular pattern of surface deformation was generated on the film. When the polarization of the laser beam is perpendicular to the edge, a regular surface relief pattern was recorded as shown in Fig. 6.

The intensity distribution on the surface of the film produced by the edge diffraction can be given by the near field diffraction theory. Fig. 7 displays the light intensity distribution and the negative of the first derivative of the light intensity. Comparing the modulation profile in Fig. 6 and negative of the first derivative of the light intensity in Fig. 7, one can clearly see that the surface profile maps the negative of the derivative of the light intensity. This can be expressed as:

$$S(x) = -\gamma \frac{dI(x)}{dx} \quad (1)$$

here  $S(x)$  is the surface profile,  $I(x)$  is the light intensity and  $\gamma$  is a constant.

By analyzing the results of recording of surface relief grating and edge diffraction pattern, we have found that there must exist light intensity variation in order to produce surface modulation. The grating grooves should be perpendicular to the light intensity gradient on the surface. Only when there is an intensity gradient in some direction with a nonzero component of the resultant electric field, the surface modulation pattern could be formed in this direction.

We have also fabricated various multiple gratings at the same spot on the film. Fig. 8 shows a typical AFM view of a grating with a well defined beat structure. This grating was recorded sequentially with two wavelengths at 488 and 514 nm at a fixed writing angle. In this case the period of the beat was about 19  $\mu\text{m}$ . It is clear that the resulting surface pattern was very close to the simple superposition of the two recording waves. Similar gratings with the beat structure can be written at two different writing angles at the same wavelength.

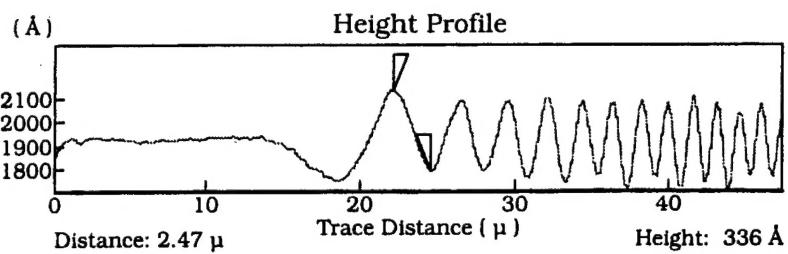


Fig. 6. AFM surface profile of the pattern on a PDO3 film produced by edge diffraction.

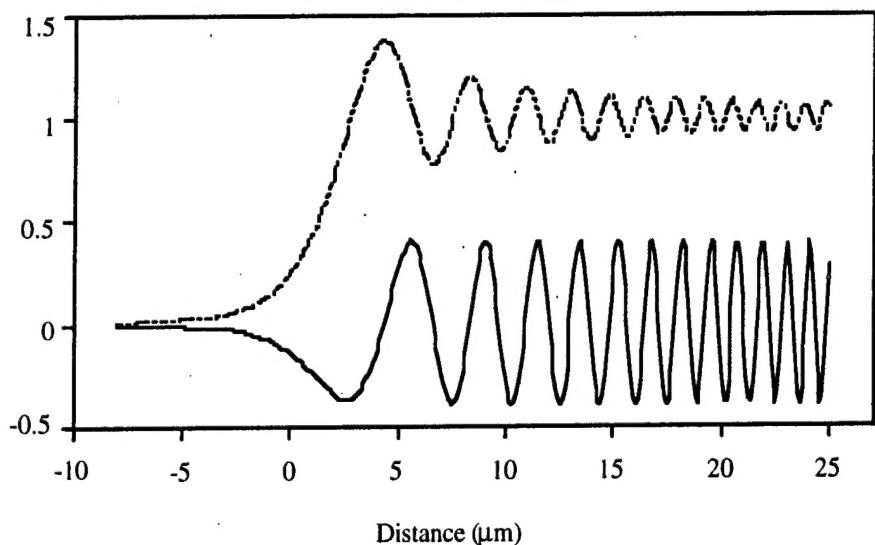


Fig. 7. Intensity distribution produced by edge diffraction (dotted line) and the negative of the first order derivative of the intensity distribution (solid line).

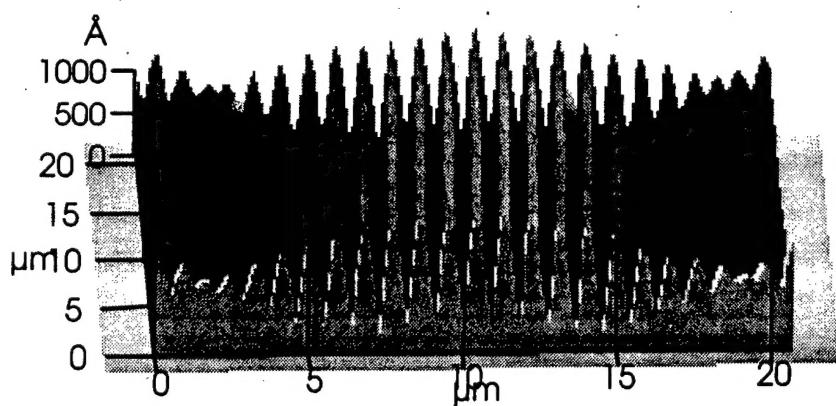


Fig. 8. AFM 3-D view of the dual gratings sequentially written with the p-polarized beams at 488 and 514 nm.

Fig. 9 shows two sets of gratings recorded orthogonally to each other on the same spot on the PDO3 film. The gratings were highly symmetric and identical that the sequence of the writing was thus not distinguishable.

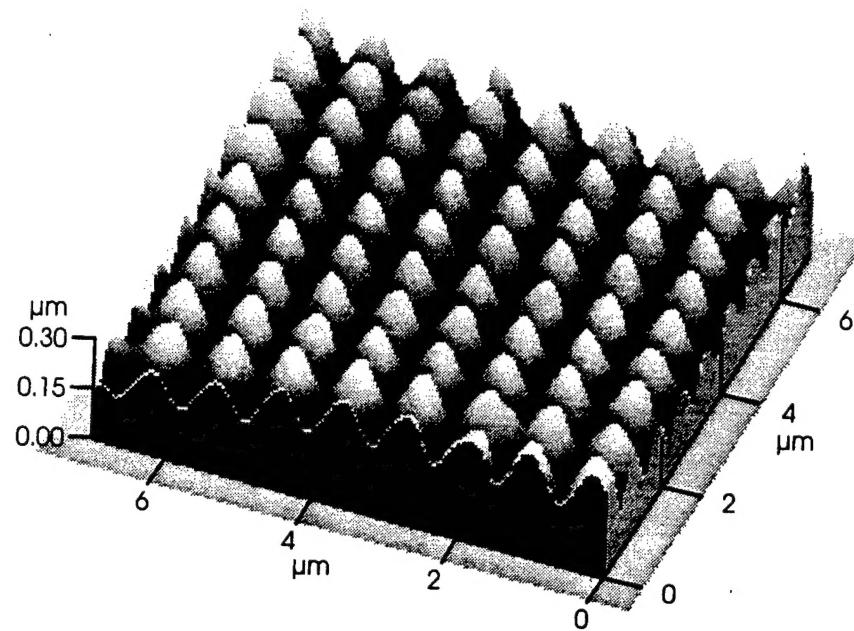


Fig. 9. AFM 3-D view of dual gratings on PDO3 film recorded orthogonally to each other.

We also fabricated a Fourier synthesized blazed grating on the polymer film by superimposing two gratings with two different spacing ( $\Lambda_g$  and  $2\Lambda_g$ ). Fig. 10 shows a typical three dimensional AFM view of a Fourier blazed grating fabricated on the PDO3 film.. The blazed structure is clearly seen. Two spatial frequency components, one at  $1/\Lambda_g$  and the other one at  $2/\Lambda_g$ , were observed as expected.

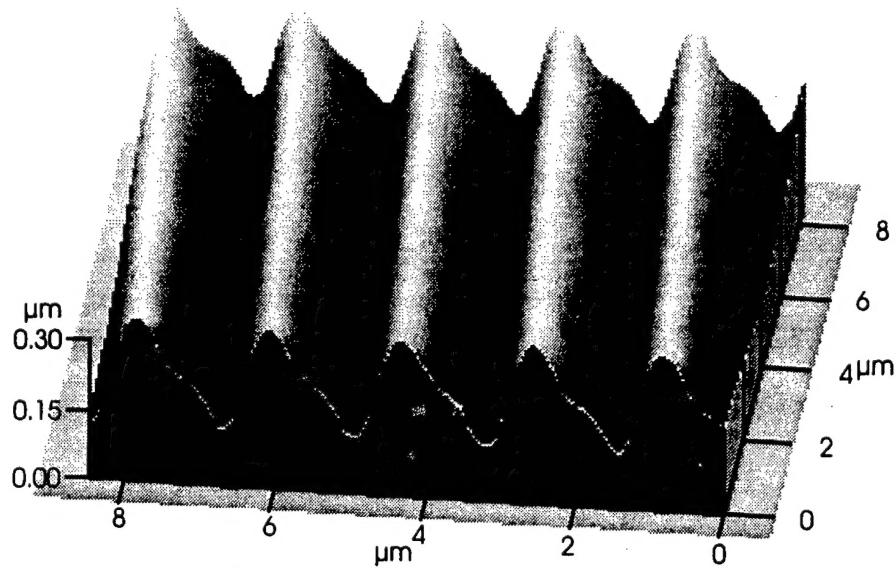


Fig. 10. A typical AFM 3-D view of a Fourier blazed grating on the PDO3 film.

#### 4. CONCLUSIONS

We have observed the formation of photo-induced surface relief gratings on various polymer films containing azobenzene groups in the side chain or in the main chain. The surface grating was not observed in the biphenyl, stilbene and imine incorporated polymers. High Tg main chain azo polymer showed slow formation of the surface grating. The rate of the grating formation depends on the Tg and optical absorption of the polymers. The recording of the gratings strongly depends on the polarization of the recording beams. Under the optimal recording conditions, surface modulation larger than 6000 Å and diffraction efficiency greater than 40 % could be achieved. The diffraction efficiency of the surface gratings was dependent only on the total light energy incident on the film. From the straight edge diffraction experiment, we have found that the surface pattern mapped the negative first derivative of the beam intensity distribution. After analyzing the resultant electric field vector distribution produced edge diffraction and by the interference of two recording beams, we believe that the existence of spatial variations of both magnitude and direction of the resultant electric field vector and nonzero component of resultant electric field along the gradient of light intensity in the films are essential conditions to induce surface modulations. We have demonstrated the formation of various multiple gratings on the same spot by simply controlling the writing wavelength and the writing angle. The resulting surface pattern was a simple superposition of all the interference recording beams regardless of the sequence of the recording. It implies that this surface grating fabrication process opens up new possibility of fabrication of complex surface optical elements and devices.

#### 5. ACKNOWLEDGMENT

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